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(54) Title: LOW TOXICITY, NON-CARCINOGENIC INHIBITORS FOR ACID PICKLING

(57) Abstract

A combination of (i) a primary inhibitor component of non-carcinogenic and low toxicity amines and/or quaternary ammonium salts with (ii) a secondary component of polarizable materials such as organic compounds containing divalent sulfur, anionic surfactants, and iodide and bromide ions has been found to give satisfactory inhibition in strong acid pickling solutions for steel, while reducing the hazard of use associated with the most used prior art pickling inhibitors.

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LOW TOXICITY, NON-CARCINOGENIC INHIBITORS FOR ACID PICKLING

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to the treatment of metal surfaces with aqueous acids to remove scale and like materials from the surface, a process commonly known in the art as "pickling", and to corrosion inhibitors used in such processes.

Statement of Related Art

Strong mineral acids such as hydrochloric and sulfuric acids, together with an inhibitor component that substantially reduces the rate of dissolution of clean metal surface from the rate that would prevail in the same type of acid solution without the inhibitor, are normally used as pickling solutions.

Advantageous inhibitors reduce the rate of dissolution of clean metal as much as possible while reducing the rate of dissolution of surface scale and like contaminating materials as little as possible. One common quantitative method of rating inhibitors used in the art, and in this description below, involves measuring the corrosion rate of

the metal to be pickled in a solution containing the type and concentration of acid used to be used for pickling, measuring the corrosion rate in a solution otherwise the same except for adding the inhibitor to be used, and then reporting the results as the percent "protection" of the inhibitor; the percent protection is defined by the following equation: $P = 100[1-(R_i/R_u)]$, where P = percent protection, R_i = corrosion rate of the metal in the inhibited solution, and R_u = the corrosion rate of the metal in the uninhibited solution, expressed in the same units as R_i.

A very wide variety of inhibitors for pickling solutions are known in the art. A useful review is given by G. Trabanelli and V. Carassiti, "Mechanism and Phenomenology of Organic Inhibitors", in *Advances in Corrosion Science and Technology*, Volume 1 (Plenum Press, New York, 1970).

Many of the most effective among the well known and frequently used inhibitors, such as propargyl alcohol and thiourea, have been reported to be carcinogenic or otherwise toxic, so that their continued use is now considered undesirable.

DESCRIPTION OF THE INVENTION

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the exact numerical limits stated is generally preferred. Furthermore, unless expressly stated to contrary below, a description of a material as selected or preferably selected from a group of specified chemical materials shall be considered to include selection from a mixture of materials each of which is a member of the stated group, and the description of an ionic material shall be understood as including necessary counterions for the specified ionic material, but without limit as to what the counterions may be unless explicitly stated. Also, the terms "solution", "soluble", and the

like are to be understood as including not only true equilibrium solutions but also dispersions that show no visually detectable tendency toward phase separation over a period of observation of at least 1000 hours.

Object of the Invention

A major object of this invention is to provide pickling inhibitors and pickling compositions that are free from carcinogens and as free as possible from otherwise toxic ingredients, while still achieving protection levels as high as possible. The desired freedom from carcinogens includes freedom from carcinogenic products formed by reaction among the components of the inhibitor within 1000 hours of mixing, as well as freedom from known carcinogens directly added to the inhibitor mixtures.

Summary of the Invention

It has been found that effective inhibition can be achieved by a combination of:

(A) a primary inhibitor selected from the group consisting of non-carcinogenic organic amines and quaternary ammonium salts, preferably those containing at least one, more preferably exactly one, alkyl group with at least 6, still more preferably at least 12, carbon atoms in each molecule of amine or quaternary ammonium salt used, said amines and quaternary ammonium salts independently preferably containing a total of at least 8, more preferably at least 15, carbon atoms per molecule; and

(B) a secondary component selected from the group consisting of non-carcinogenic (i) organic compounds that contain divalent sulfur atoms and are not amines or quaternary ammonium salts, (ii) anionic organic surfactants that are not amines or quaternary ammonium salts, (iii) iodide and bromide ions, and (iv) polymaleic acid.

One major embodiment of the invention is a concentrate useful for adding to aqueous acid solutions to produce a working pickling solution. A second major embodiment is a

working pickling solution containing a combination inhibitor component according to the invention, and a third major embodiment is a process of pickling with such a working pickling solution.

Description of Preferred Embodiments

A concentrate according to the invention is preferably liquid at 25° C, and independently, preferably contains amounts of components (A) and (B) that are mutually interrelated to produce a synergistic effect, i.e., so that the percent inhibition value as already defined above is greater for the combination A_a + B_b than for either A_a or B_b alone, where capital letters represent the composition selected from the group designated with the same capital letter in parentheses as defined above and lower case subscripts represent the quantitative concentration of the composition represented by the captial letter to which they are appended. Thus, for example, A_a represents a concentration "a" of a particular selection "A" from the group "(A)" as defined above and B_b represents a concentration "b" of a particular composition "B" from the group "(B)" as defined above. Still more preferably, the combination A_a + B_b has a greater percent inhibition than either $A_{(a+b)}$ or $B_{(a+b)}$.

Optional ingredients that are often useful in concentrates according to the invention are (C) acid to promote solubility of the amines used, (D) organic solvents, when needed for solubility, and (E) nonionic and cationic organic surfactants. Preferably, a concentrate according to the invention consists essentially of, or still more preferably consists of, necessary components (A) and (B) and, optionally, of one or more of optional components (C), (D), (E), and water.

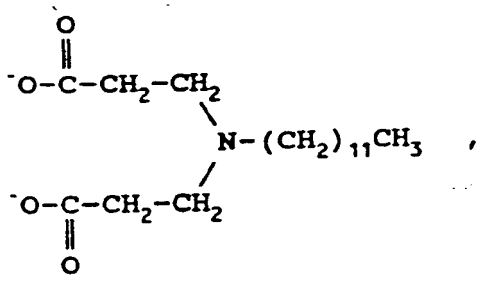
Preferable amounts and chemical characteristics for components (A) and (B) depend to some extent on the pickling acid with which the inhibitor is used, or in the case of a concentrate, intended to be used. A concentrate according to the invention to be used with a hydrochloric

acid based pickling solution preferably contains necessary component (A) as described above in an amount within the range from 5 to 50, more preferably from 15 to 35, or still more preferably from 24 to 30, % by weight; and, independently, preferably contains necessary component (B) as described above in an amount within the range from 2.0 to 16, more preferably from 4 to 12, or still more preferably from 6 to 10, % by weight. (All per cent values herein are by weight unless otherwise specified, and any specified percentage or ratio is for the ingredient or component as specified chemically or by trade name only, not including any solvent, counterions, or the like when the percentage specified is for a chemical or chemical class. On the other hand, when the specification is for a tradenamed product, the percentage or other quantitative specification refers to the product as sold.)

Independently, with or for hydrochloric acid, it is preferable for component (A) to include both a quaternary ammonium salt and an amine, in a ratio by weight of the amine to the quaternary ammonium salt in the range from 30:1 to 6:1, more preferably from 25:1 to 9:1, still more preferably from 18:1.0 to 14:1.0; and it is independently preferred, with increasing preference in the order stated, that at least 6, 11, 15, 24, 31, or 40 % of component (A) in a composition according to this invention would consist of amines including a pyridine ring structure. Independently, with hydrochloric acid, it is preferred that the quaternary ammonium salt contain aryl and/or alkyl substituents and/or that the amine be an abietylamino-oligo(oxyethylene)ethanol, with the average number of oxyethylene groups per molecule most preferably being in the range from 5 to 11.

Also and independently, with hydrochloric acid, it is preferred that component (B) include both anionic organic surfactants and iodide ions, in a ratio by weight within the range from 26.4:1.0 to 1.3:1.0, more preferably from 11.6:1.0 to 2.3:1.0, still more preferably from 4.6:1.0 to

3.3:1.0. Preferably, the anionic part of the anionic surfactant is selected from anions comprising at least one nitrogen atom, more preferably from the group consisting of 2-caprylic-1-(ethyl β-oxypropanoate)imidazoline, N-(1,2-dicarboxylateethyl)-N-octadecylsulfosuccinimate, and N-lauryliminodipropionate, which the following chemical formula for the anion:



the latter anion being the most preferred.

For sulfuric acid pickling, a concentrate according to the invention preferably contains necessary component (A) as described above in an amount within the range from 5 to 50, more preferably from 10 to 30, or still more preferably from 15 to 22, % by weight; and, independently, a concentrate for use in sulfuric acid based pickling solutions preferably contains necessary component (B) as described above in an amount within the range from 0.5 to 10, more preferably from 1.0 to 8, or still more preferably from 2.0 to 6.0, % by weight. Also, it is independently preferred, with increasing preference in the order stated, that at least 35, 53, 67, 81, or 90 % of component (A) in a composition according to this invention would consist of amines including a pyridine ring structure.

Also and independently, for use with sulfuric acid, it is preferred, with increasing preference in the order stated, that at least 35, 53, 67, 81, or 90 % of component (B) in a composition according to this invention would consist of diarylthiourea molecules, most preferably of N,N'-diphenylthiourea; and, independently, that the ratio by weight of component (A) to component (B) fall within the range from 10:1 to 1:1, more preferably from 6.0:1.0 to

2.0:1.0, or still more preferably from 4.6:1.0 to 3.5:1.0.

Also and independently, with sulfuric acid, it is preferred that the inhibitor composition according to this invention include alkylaryl-oligo{oxyethylene}ethanol nonionic surfactant, which in a concentrate is preferably present in an amount within the range from 3 to 15, more preferably from 4 to 10, or still more preferably from 5.0 to 7.5, % by weight, and, independently, is preferably present in an amount such that the ratio by weight of this type of nonionic surfactant to component (A) falls within the range from 0.05:1.0 to 1.0:1.0, more preferably from 0.1:1.0 to 0.6:1.0, or still more preferably from 0.21:1.0 to 0.40:1.0.

A working pickling solution according to this invention preferably contains from 5.0 to 36, more preferably from 7.0 to 30, or still more preferably from 10.0 to 28.8, % of acid, preferably selected from hydrochloric acid, sulfuric acid, alkali metal bisulfates, phosphoric acid, oxalic acid, formic acid, citric acid, acetic acid, tartaric acid, hydroxyacetic acid, sulfamic acid, and mixtures thereof; more preferably, the acid is either sulfuric or hydrochloric. A working pickling solution according to the invention also and independently preferably contains from 0.010 to 1.0, more preferably from 0.030 to 0.50, or still more preferably from 0.050 to 0.20, % of a concentrate inhibitor composition according to the invention as already described above.

A process according to the invention comprises contacting a metal workpiece to be pickled with a working pickling solution according to the invention as described above, preferably at a temperature in the range from 16 to 93, more preferably from 52 to 88, or still more preferably from 66 to 82, ° C for a time sufficient to remove scale and other bulk oxide coatings from the workpiece surface; independently, the time of contact preferably is in the range from 10 to 60, more preferably from 15 to 45, or still more preferably from 25 to 35, minutes, although the

time naturally will vary considerably as a function of the amount and type of surface contamination to be removed. Contact between the workpiece and the working pickling solution is generally by immersion, but any process of establishing the requisite contact, as known *per se* in the art, may be used.

The practice and benefits of the invention may be further appreciated by consideration of the following non-limiting working and comparison examples.

Examples and Comparison Examples of Pickling with Working Compositions

Group 1

In all these cases, the basic pickling solution was 14 % hydrochloric acid used for 30 minutes (hereinafter often abbreviated "min") at 82° C and the workpieces were Type 4140 alloy steel. Some percent protection values achieved with individual inhibitors and with a combination of these inhibitors are shown in Table 1.

Table 1
PICKLING IN 14 % HYDROCHLORIC ACID FOR 30 MIN AT 82°

Ingredient	Percent in Solution	Percent Protection
WITCAMINE™ RAD-1100 (reported by its manufacturer to be abiethyl amine with an average of 11 ethylene oxide units per molecule)	0.1	93.0
DERIPHAT™ 160 (disodium N-lauryl iminodipropionate)	0.05	0
WITCAMINE™ RAD 1100 and DERIPHAT™ 160	0.1 } 0.05 }	96.6

Group 2

This group was treated under the same conditions as Group 1, except that the workpieces were cold rolled steel and the temperature of the pickling solution was 66° C. Without any inhibitor, the corrosion rate of the steel under these conditions was 60 centimeters (hereinafter often

abbreviated "cm") per year (hereinafter often abbreviated "yr"). Results are shown in Table 2.

Table 2
PICKLING IN 14 % HYDROCHLORIC ACID FOR 30 MIN AT 66°

Ingredient	Percent in Solution	Percent Protection
Tetrabutyl ammonium chloride	0.1	0
Poly(maleic acid)	0.1	0
Tetrabutyl ammonium chloride and Poly(maleic acid)	0.1 0.1	96.5
Trimethyldodecyl ammonium chloride	0.025	84.1
Ammonium thiocyanate	0.1	0
Tetrabutyl ammonium iodide	0.0075	30.3
Trimethyldodecyl ammonium chloride + Ammonium thiocyanate	0.05 0.1	93.8
Trimethyldodecyl ammonium chloride + Tetrabutyl ammonium iodide	0.05 0.1	96.4

Group 3

The general conditions for this group were the same as for Group 2, except that the acid used was 10 % sulfuric acid instead of 14 % hydrochloric, and the corresponding corrosion rate without any inhibitor was 50.5 cm/yr. Some results illustrating synergism and some comparison results are shown in Table 3.

Table 3
PICKLING IN 10 % SULFURIC ACID FOR 30 MIN AT 66°

Ingredient	Percent in Solution	Percent Protection
N,N'-diphenyl thiourea	0.05	92.2
AKOLIDINE™ 12 (reported by its manufacturer to be a mixture of alkyl pyridines)	0.05	70.1
Thiodiglycolic acid	0.1	0
ETHOQUAD™ c/25 (reported by its manufacturer to be a polyethoxylated quaternary ammonium chloride)	0.1	84.5
N,N'-diphenyl thiourea and AKOLIDINE™ 12	0.009 / 0.04	99.3
N,N'-diphenyl thiourea and ETHOQUAD™ c/25	0.0012 / 0.025	98.0
Thiodiglycolic acid and ETHOQUAD™ c/25	0.05 / 0.04	96.5

Examples of Concentrate Compositions According to the Invention

Example 4.1

A concentrate composition particularly well suited to use with sulfuric acid based pickling solutions, but also suitable for use with other acids, has the following composition:

Ingredient	Percent by Weight in Concentrate
AKOLIDINE™ 12	18.6
Water	18.6
Concentrated sulfuric acid (95 - 98 %)	5.9
TRITON™ N-101	6.5
Propylene glycol	24.6
2-Phenoxyethanol	21.5
N,N'-diphenylthiourea	4.3

AKOLIDINE™ 12 is commercially available from Lonza, and as already noted is a mixture of alkyl pyridines. TRITON™ N-101 is commercially available from Union Carbide and is described by its manufacturer as a "Nonylphenoxy polyethoxy ethanol" with a Hydrophile-Lipophile Balance value of 13.4.

In this concentrate composition propylene glycol and 2-phenoxyethanol are believed to function essentially only as solvents, while TRITON™ N-101 also functions predominantly as a solvent but is believed to contribute at least slightly to the inhibition also. The acid is believed to aid solubility of the AKOLIDINE™ 12 by forming at least a partial salt with it. The primary inhibiting ingredients are the AKOLIDINE™ 12, corresponding to component (A) in the general description of the invention above, and the N, N'-diphenylthiourea, corresponding to component (B)(i) in the general description above.

Example 4.2

A concentrate composition particularly well suited to use with hydrochloric acid based pickling solutions has the following composition:

Ingredient	Percent by Weight in Concentrate
AKOLIDINE™ 12	12.0
Water	60.0
Concentrated phosphoric acid (75 %)	5.0
DODICOR™ 2565	3.0
WITCAMINE™ RAD 1100	12.0
Potassium iodide	2.0
DERIPHAT™ 160	6.0

DODICOR™ 2565 is commercially available from Hoechst-Celanese Corp. and is described by its manufacturer as an aryl alkyl quaternary ammonium chloride. WITCAMINE™ RAD 1100 is commercially available from Witco Corp.; the chemical description given by its manufacturer is shown in Table 1. DERIPHAT™ 160 is available from Henkel Corporation, COSPHA Div.; it is a dry powder of a partial sodium salt of

N-lauryl iminodipropionate.

In this concentrate composition, the AKOLIDINE™ 12, DODICOR™ 2565, and WITCAMINE™ RAD 1100 jointly constitute component (A) as defined in the general description of the invention above, while the potassium iodide and the DERIPHAT™ 160 C jointly constitute component (B) as defined in the general description of the invention above.

Corrosion rates and degrees of inhibition found with 30 min of pickling of cold rolled steel in 10 % sulfuric acid inhibited with these concentrates are shown in Table 4.

Table 4
CORROSION RATES AND PERCENT PROTECTION WITH EXAMPLES 4.1 - 4.4

Inhibitor		Corrosion in cm/yr		Percent Protection	
Example Number	Concentration in Working Pickling Solution	At 66° C Pickling Temperature	At 82° C Pickling Temperature	At 66° C Pickling Temperature	At 82° C Pickling Temperature
4.1	0.1 %	0.35	1.54	99.3	98.7
4.2	0.1 %	0.30	1.66	99.4	98.6

The invention claimed is:

3. A composition according to claim 2, wherein component (A) is present in a concentration in the range from about 15 to about 35 % and includes both a quaternary ammonium salt and an amine in a ratio by weight of the quaternary ammonium salt to the amine in the range from about 30:1 to about 6:1, and component (B) is present in a concentration in the range from 4 to 12 % and includes both anionic organic surfactants and iodide ions in a ratio by weight of the anionic organic surfactants to the iodide ions in the range from 11.6:1.0 to 2.3:1.0.

4. A composition according to claim 3, wherein component (A) is present in a concentration in the range from about 24 to about 30 %, includes both a quaternary ammonium salt and an amine in a ratio by weight of the quaternary ammonium salt to the amine in the range from about 18:1 to about 14:1, and comprises amines having a pyridine ring structure to an extent of at least 24 % of the total amount of component (A); and component (B) is present in a concentration in the range from 6 to 10 %, includes both anionic organic surfactants and iodide ions in a ratio by weight of the anionic organic surfactants to the iodide ions in the range from 4.6:1.0 to 3.3:1.0, the anionic parts of said anionic surfactants containing at least one nitrogen atom per molecule.

5. A composition according to claim 4, wherein at least 40 % of component (A) consists of molecules including a pyridine ring structure and the anionic parts of the anionic surfactants present in component (B) are selected from the group consisting of 2-caprylic-1-(ethyl β-oxypropanoate)imidazoline,N-(1,2-dicarboxylateethyl)-N-octadecylsulfosuccinimate, and N-lauryliminodipropionate.

CLAIMS

1. A composition of matter free from carcinogenic materials and consisting essentially of:

(A) a primary inhibitor selected from the group consisting of organic amines, salts thereof, quaternary ammonium salts, and mixtures of any two or more thereof; and

(B) a secondary component selected from the group consisting of (i) organic compounds that contain divalent sulfur atoms and are not amines or quaternary ammonium salts, (ii) anionic organic surfactants that are not amines or quaternary ammonium salts, (iii) iodide and bromide ions, and (iv) polymaleic acid; and, optionally,

(C) a component of acid to form salts with any amines used; and, optionally,

(D) a component of one or more organic solvents; and, optionally,

(E) a component selected from nonionic and cationic organic surfactants and mixtures of any two or more thereof; and, optionally,

(F) water,

said composition of matter having the property that a solution of a selected concentration of it in at least one inorganic acid selected from the group consisting of sulfuric, hydrochloric, and phosphoric acids and mixtures thereof has a higher percentage protection against corrosion of steel than either of otherwise identical solutions from which either component (A) or component (B) only is replaced by an equal amount of the inorganic acid.

2. A composition according to claim 1, wherein the concentration of component (A) is in the range from about 5 to about 50 % and the concentration of component (B) is in the range from about 2 to about 16 %.

6. A composition according to claim 5, consisting essentially of about 12 % of alkyl pyridines, about 3.8 % of phosphoric acid, about 3.0 % of alkylaryl quaternary ammonium salt, about 12 % of abiethyl amine with an average of about 11 ethylene oxide units per molecule, about 2 % of potassium iodide, and about 1.8 % total of sodium and disodium N-lauryliminodipropionate, with the balance being water.

7. A composition according to claim 1, wherein the concentration of component (A) is in the range from about 5 to about 50 % and the concentration of component (B) is in the range from about 0.5 to about 10 %.

8. A composition according to claim 7, wherein the ratio by weight of component (A) to component (B) is in the range from about 6.0:1.0 to 2.0:1.0, at least about 67 % of component (A) consists of amines having a pyridine ring structure, at least about 53 % of component (B) consists of diarylthiourea molecules and the composition includes from about 3 to about 15 % of alkylaryl-oligo(oxyethylene)ethanol nonionic surfactant.

9. A composition according to claim 8, wherein the concentration of component (A) is in the range from about 10 to about 30 %, the concentration of component (B) is in the range from about 1.0 to about 8 %, at least 67 % of component (B) consists of diarylthiourea molecules, the concentration of alkylaryl-oligo(oxyethylene)ethanol nonionic surfactant is in the range from about 4 to about 10 % and the ratio by weight of alkylaryl-oligo(oxyethylene)ethanol nonionic surfactant to component (A) is in the range from about 0.1:1.0 to 0.6:1.0.

10. A composition according to claim 9, wherein the concentration of component (A) is in the range from about 15 to about 22 %, the concentration of component (B) is in the range from about 2.0 to about 6.0 %, at least 81 % of component (A) consists of amines having a pyridine ring structure, at least 81 % of component (B) consists of diarylthiourea molecules, the concentration of alkylaryl-oligo(oxyethylene)ethanol nonionic surfactant is in the range from about 5.0 to about 7.5 % and the ratio by weight of alkylaryl-oligo(oxyethylene)ethanol nonionic surfactant to component (A) is in the range from about 0.21:1.0 to 0.40:1.0.

11. A composition according to claim 10, consisting essentially of about 18.6 % of alkyl pyridines, about 5.8 % of sulfuric acid, about 6.5 % of nonylphenoxylpoly(ethoxy)ethanol, about 24.6 % of propylene glycol, about 21.5 % of 2-phenoxyethanol, and about 4.3 % of N,N'-diphenylthiourea, with the balance water.

12. A process for pickling a metal workpiece in an acidic aqueous pickling solution comprising from about 5.0 to about 36 % of acid and from about 0.010 % to about 1.0 % of a composition according to claim 1.

13. A process according to claim 12, wherein the acid is selected from the group consisting of hydrochloric acid, sulfuric acid, alkali metal bisulfates, phosphoric acid, oxalic acid, formic acid, citric acid, acetic acid, tartaric acid, hydroxyacetic acid, sulfamic acid, and mixtures thereof, the temperature of the pickling solution during the process is within the range from about 16 to about 93 ° C.

14. A process according to claim 13, wherein the workpiece is steel, the acid includes hydrochloric acid in a concentration in the range from about 7.0 to about 30 %, the temperature of the pickling solution during the process is within the range from about 52 to about 88 ° C, and the pickling solution comprises a concentration within the range from about 0.030 to about 0.50 % of a composition according to claim 4.

15. A process according to claim 14, wherein the acid includes hydrochloric acid in a concentration in the range from about 10.0 to about 28.8 %, the temperature of the pickling solution during the process is within the range from about 66 to about 82 ° C, and the pickling solution comprises a concentration within the range from about 0.020 to about 0.20 % of a composition according to claim 5.

16. A process according to claim 15, wherein the pickling solution comprises a concentration within the range from about 0.020 to about 0.20 % of a composition according to claim 6.

17. A process according to claim 13, wherein the workpiece is steel, the acid includes sulfuric acid in a concentration in the range from about 7.0 to about 30 %, the temperature of the pickling solution during the process is within the range from about 52 to about 88 ° C, and the pickling solution comprises a concentration within the range from about 0.030 to about 0.50 % of a composition according to claim 8.

18. A process according to claim 17, wherein the acid includes sulfuric acid in a concentration in the range from about 10.0 to about 28.8 %, the temperature of the pickling solution during the process is within the range from about 66 to about 82 ° C, and the pickling solution comprises a concentration within the range from about 0.020 to about 0.20 % of a composition according to claim 9.

19. A process according to claim 18, wherein the pickling solution comprises a concentration within the range from about 0.020 to about 0.20 % of a composition according to claim 10.

20. A process according to claim 19, wherein the pickling solution comprises a concentration within the range from about 0.020 to about 0.20 % of a composition according to claim 11.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07128

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/136, 143, 146, 148, 149, 151, 153, 166, 174.21, 174.22, 524, 526, 528, 542, 544, 545, 547

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US, A, 4,541,945 (Anderson et al.) 17 September 1985 See col. 2, lines 10-12, lines 44-55; col. 3,. lines 12-38, lines 50-66; col. 4, lines 4-13, lines 17-34; col. 6, line 22.	1,2, 7 & 12-20 1-20
Y	US, A, 3,668,137 (Gardner) 06 June 1972 see col. 2, lines 30-47.	1-20
Y	US, A, 4,780,150 (Anderson et al.) 25 October 1988 see col. 3, lines 39-50.	1-20
Y	US, A, 4,292,190 (Davis et al.) 29 September 1981 see col. 2, lines 28-32, lines 58-65.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 01 SEPTEMBER 1993	Date of mailing of the international search report 25 OCT 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer PAUL LIEBERMAN Telephone No. (703) 308-2520

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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER:
IPC (5):

C11D 1/86, 1/94, 3/04, 3/16, 3/18, 3/20, 3/28, 3/30, 3/34 3/43, 3/44; C23G 1/06, 1/08.

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

252/136, 143, 146, 148, 149, 151, 153, 166, 174.21, 174.22, 524, 526, 528, 542, 544, 545, 547.